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Morember, 1996.

Sherry Cardwell

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Serial No.: 08/224,961 (Attorney Docket No. U/M 939)

Filed: April 8, 1994

Mourou et al.

Group 2106

Examiner: G. Evans

DECLARATION TRAVERSING GROUNDS OF REJECTIONS UNDER 37 CFR §1.132 OF PETER P. PRONKO

Assistant Commissioner for Patents Washington, D.C. 20231

- I, Peter P. Pronko, hereby declare as follows:
- 1. I, Peter P. Pronko, am one of the persons named as a joint inventor in the above-identified U.S. Application Serial No. 08/224,961 filed April 8, 1994.

- 2. Peter P. Pronko received a Bachelor of Science Degree in Physics from the University of Scranton in Pennsylvania; a Master of Science Degree in Physics from the University of Pittsburgh in Pennsylvania; and a Ph.D. Degree in Physics from the University of Alberta in Canada. During the time of conception and actual reduction to practice of the invention of the present application, Peter P. Pronko, was employed by the University of Michigan, Ann Arbor, Michigan, as a Research Scientist for Ultrafast Optics at the University of Michigan's Center for Ultrafast Optical Science. Peter P. Pronko has been named as a joint inventor in several patents; is an author or co-author in over 100 publications; and has been a presenter or joint presenter at over 200 conferences. A curriculum vitae is attached.
- 3. I have carefully read and understood Miyauchi et al, U.S. Patent No. 5,208,437; Herziger et al, U.S. Patent No. 4,839,493; Zinck et al, U.S. Patent No. 5,454,902; Kunz et al, U.S. Patent No. 4,675,500; and Von Allmen et al, U.S. Patent No. 4,114,018.
- 4. Examiner has rejected independent claims 1, 21, and 40 and dependent claims 5, and 8 11, and 13 17, and 22 through 28 on the basis of Miyauchi, U.S. Patent No. 5,208,437. Examiner states that "Miyauchi discloses laser heating of Aluminum of cutting at less than one nanosecond which is less than the threshold of fluence for Aluminum." Examiner makes the supposition that such cutting is at less than the threshold fluence for aluminum on the basis of Herziger, U.S. Patent No. 4,839,493, saying that Herziger "shows that plasma does not occur until the workpiece is at or above its evaporation temperature."

- 5. In referencing Herziger, the Examiner states that the plasma does not form until the workpiece is at or above the evaporation temperature for the laser parameters as described in that reference. Based on this premise, he goes on to state that Miyauchi must be operating at a pulse duration that is less than the pulse width at which there is a change in slope of the threshold fluence versus pulse width curve.
- data referenced in Herziger is simply incorrect in rejecting claims to the present invention. Examiner is assuming that the only way to make a plasma is by heating a material to a temperature above its formation evaporation temperature. This assumption coincides with conventional thinking as per Miyauchi and Herziger. The present invention teaches a surprisingly effective new approach where plasma forms below the melting or evaporation temperature.
- 7. In the present invention, plasmas are formed by exposing material to very intense electrical fields. This is, in fact, the preferred way to form a plasma as taught by the present That is, by using the intense electric field of the invention. laser pulse. The present invention teaches <u>laser induced breakdown</u> (LIB) which is defined in the patent application, and is dielectric breakdown and plasma formation resulting from multiphoton ionization, avalanche or ionization, or barrier tunneling ionization, or spontaneous auto-ionization, or various combinations of these. The cited art does not remotely suggest LIB. short pulse laser-matter interaction of the invention, laser energy absorbed by electrons raises the electron temperature to a very high value in a very short time, forming a plasma, while the lattice temperature remains relatively cold, below the melting or evaporation temperature.

- 8. According to the present invention, the electric field causes a dielectric breakdown of the material and plasma formation resulting from multiphoton ionization, or avalanche ionization, or barrier tunneling ionization, or spontaneous autoionization, or various combinations of these. The presence of this plasma, once formed, is to provide a medium which can undergo a certain amount of hydrodynamic expansion thereby providing an ablative source, or it may also act as a heating source (prior to and/or during expansion) that can cause the temperature of the surrounding material from which it was formed to be increased so that the evaporation occurs AFTER THE PLASMA WAS FORMED. This reverses the logic of the applied art and of the Examiner and, therefore, of necessity reverses the basis for rejection stated in the Office Action.
- The various patents and references the Examiner is citing are for long pulse duration and, therefore, for low laser intensity (10° to 10° watts/cm²) and low electric field conditions. These conditions are not relevant to the method of the invention. The conditions of the cited art cannot produce laser induced breakdown (LIB), which is defined in the patent application, and is dielectric breakdown and plasma formation resulting multiphoton ionization, or avalanche ionization, or tunneling ionization, or spontaneous auto-ionization, or various combinations of these. The cited art does not remotely suggest LIB.
- 10. The present invention relies on short pulses and, therefore, much higher intensities (> 1011 watts/cm2) and, therefore, high electric field conditions, resulting in LIB as defined above and in the present patent application.

- opposite to the method of the Miyauchi patent is directly opposite to the method of the present invention, since Miyauchi relies exclusively on the concept of a 1/th dependence of a thermal threshold fluence for melting or evaporation to achieve ablation effect. (See discussion in Miyauchi at Col. 2 at lines 30-45.) This means by definition that they are operating in the region of the damage fluence curve that is completely different from the defined "abrupt and distinct change of slope" region of the present invention. The present invention relies on the use of fluences that are below this point. The significance of this point, that we identified on the damage fluence curve is that it defines the stage at which a transition from thermally controlled processes give way plasma controlled effects, LIB, laser induced breakdown.
- 12. It bears repeating that, <u>for the first time</u>, by our invention we have identified the region on the damage fluence curve that <u>defines</u> the stage at which a transition from thermally <u>controlled process gives way to plasma controlled effects</u>, <u>LIB</u>, laser induced breakdown.
 - 13. Miyauchi et al have completely missed this point.
- 14. In contrast to Examiner's interpretation, Col. 2 lines 30-40 of Miyauchi clearly states the square root relationship between power (intensity) and pulse width, with NO LIMIT on pulse width ranges, and no suggestion of "LIB" and "plasma formation". These terms are not mentioned anywhere in Miyauchi. Miyauchi did not reach LIB at all. Further, although Miyauchi states a laser pulse of "1 nanosecond or less", in Col. 3 at line 35, he specifies "100 to 300 picoseconds". This is well outside the 10 femtoseconds to 10,000 femtoseconds (10 picoseconds) of the present invention.

Note here that Miyauchi's 100 to 300 picoseconds at Col 2 at lines 59-62 is for the material "made of aluminum or the like." Clearly, Miyauchi's range was meant to be exemplary for a metal, evidencing Miyauchi's inability to achieve LIB as defined by the present invention.

- 15. In contrast, the present invention contradicts Miyauchi and conventional thinking by new data. This new data demonstrates that for a metal, such as Al and Au, LIB mechanism as defined in the items above, and in the present invention, occurs at a laser pulse well outside Miyauchi's 100 to 300 picoseconds. Miyauchi never suggested the femtosecond range of the present invention necessary to achieve LIB mechanism; and identified only by the present invention's "change of slope" characterization.
- 16. The present invention relies upon the production of a spontaneous plasma formed by LIB to effect the ablation, and recognizes that thermal effects are virtually eliminated from the process when operating near the threshold. Therefore, the present invention deviates completely from the 1/th behavior as exemplified in Miyauchi. This plasma process occurs when one operates below the critical point defined by the present invention's "distinct and abrupt change of slope" in the damage fluence versus pulse width threshold curve. The present invention, for the first time, specifically teaches that one should avoid doing what Miyauchi et al teach. That is to say, the present invention avoids thermal based (1/t) behavior entirely. In contrast, Miyauchi relies on such thermal ablation process. (See Miyauchi at Col. 2 at lines 30-45.)

- 17. operating in accordance with conventional teaching, Miyauchi does not avoid thermal diffusion effects and disruptive energy delivered into the bulk material surrounding the area desired to be ablated. Therefore, Miyauchi cannot minimize collateral damage. This is accomplished, for the first time, only by the present invention. Miyauchi et al admit that their method cannot effectively minimize collateral damage. Based on the teaching of the present invention, we now know why Miyauchi has failed in this regard. Miyauchi et al have misunderstood and misdefined the pulse duration at which damaging, collateral thermal effects are significant. Referring to Col. 2 beginning at line 59, it states that "It takes about 1 nanosecond for the laser energy to be transformed into heat within the interconnection pattern made of aluminum or the like." The implication here is that at 100 to 300 picoseconds no significant thermal processes are occurring. This is simply wrong. For metals, such as aluminum, gold, and the like, we, for the first time, have demonstrated that the pulse duration must go below approximately 10 picoseconds for thermal effects to be significantly minimized. Therefore, for the first time, we now understand why Miyauchi has not been able to avoid collateral damage. That is because Miyauchi teaches to operate in the 1/th regime at 100 to 300 picoseconds as stated in their discussion at Col. 2 at lines 40-45.
- 18. Clearly, Miyauchi is stating that according to the conventional thinking, in the case of a metal, he states "aluminum and the like," it is sufficient to operate in a range of 100 to 300 picoseconds. Again, this is <u>outside</u> the present invention's femtosecond range.

- In summary, rejection of independent claims 1, 21, and 40 and dependent claims 5, and 8 - 11, and 13 - 17, and 22 through 28 is unsupportable and inappropriate. This is at least because the Examiner's interpretation of Miyauchi based on data referenced in Herziger is simply incorrect in rejecting claims to the present invention. Examiner is assuming that the only way to make a plasma is by heating a material to a temperature above its formation evaporation temperature. This assumption coincides with conventional thinking as per Miyauchi and Herziger. The present invention teaches a surprisingly effective new approach where plasma forms below the melting or evaporation temperature. In the present invention, plasmas are formed by exposing material to very intense electrical fields. This is, in fact, the preferred way to form a plasma as taught by the present invention. That is, by using the intense electric field of the laser pulse. The present invention teaches <u>laser induced breakdown (LIB)</u> which is defined in the patent application, and is dielectric breakdown and plasma formation resulting from multiphoton ionization, or avalanche ionization, or barrier tunneling ionization, or spontaneous autoionization, or various combinations of these. The cited art does not remotely suggest LIB. In the short pulse laser-matter interaction of the invention, laser energy absorbed by electrons raises the electron temperature to a very high value in a short time, forming a plasma, while the lattice temperature remains relatively cold, below the melting or evaporation temperature.
- opposite to the method of the Miyauchi patent is directly opposite to the method of the present invention, since Miyauchi relies exclusively on the concept of a 1/t dependence of a thermal threshold fluence for melting or evaporation to achieve ablation effect. (See discussion in Miyauchi at Col. 2 at lines 30-45.) This means by definition that they are operating in the region of

the damage fluence curve that is <u>completely different</u> from the defined "abrupt and distinct change of slope" region of the present invention. The present invention relies on the use of fluences that are below this point. The significance of this point, that we identified on the damage fluence curve is that it defines the stage at which a transition from thermally controlled processes give way plasma controlled effects, LIB, laser induced breakdown. It bears repeating that, <u>for the first time</u>, by our invention we have identified the region on the damage fluence curve that <u>defines</u> the stage at which a transition from thermally controlled process gives way to plasma controlled effects, LIB, laser induced <u>breakdown</u>. Miyauchi et al have completely missed this point.

- 21. Independent claims 1 and 21 and dependent claims 8 through 11, 13 through 17, and 22 through 28 were rejected on the basis of Zinck. It is respectfully submitted that in the Office Action Zinck is completely misinterpreted.
- 22. Zinck's patent is for processing Cd/Te semiconductor material. The Office Action states "Zinck et al in U.S. Patent No. 5,454,092 performs ablation below the threshold fluence; consequently, Zinck et al must be using pulses for its power level that are less than the pulse width at which there is a change in slope of the threshold fluence versus pulse width."
- 23. Zinck et al are misusing the term "ablation". Zinck et al are not performing an ablation procedure at all. Zinck et al are clearly not performing any operation associated with LIB. Zinck is performing a procedure to cause a change in stoichiometry. (See Zinck at Col. 3 at lines 31-35 wherein it is stated "The existence of a threshold fluence (about 40 mJ per cm²) above which the Cd/Te surface stoichiometry is altered is shown in Figure 1."

- 24. Clearly, Zinck has prepared a curve of the ratio of Cd atoms to Te atoms as a function of laser fluence. This has absolutely nothing to do with laser induced breakdown, LIB. This is obvious, because Zinck provides no pulse width dependence of any kind.
- 25. In other words, Zinck et al is based on a concept of surface desorption and low temperature evaporation of loosely bound atoms from the surface. This is a surface cleaning and reordering process that involves atomic surface diffusion on a small scale of less than 10 atomic layers in thickness. The threshold the Examiner refers to is a threshold for preferential desorption of tellurium atoms from the surface.
- 26. Zinck specifically teaches that the laser fluence should not exceed "about 75 mJ per cm², in order to avoid melting of the Cd/Te surface." See Zinck at Col. 3 at lines 28-30. It is clear that Zinck is operating in a desorption/surface annealing mode. Zinck is restricted to nanosecond laser pulses exclusively. Clearly, nanosecond laser pulses are well outside the range required and defined by the invention of our present application.
- 27. The rejection based on Zinck is really inappropriate and incomprehensible. Zinck does not discuss pulse width at all. Zinck is only concerned about energy fluence levels related to preferential surface annealing. This is totally unrelated to the present invention which defines preferred threshold fluence for LIB mechanism. Whereas, Zinck's process involves thermal annealing which makes the surface Cd rich in the process and preferentially removes excess Cd, the present invention has nothing to do at all with thermal annealing and desorption phenomena.

- 28. In summary, Zinck et al contains a relationship between Cd/Te ratio obtained by thermal anneal as a function of laser fluence. In contrast, the present invention is concerned with the process for laser induced breakdown (LIB) involving a relationship between the damage fluence versus laser pulse width. Simply by comparing the relationships defined in Zinck and the present application, it is abundantly clear, even to those unskilled in the art, that a curve of stoichiometry/thermal anneal versus laser fluence has absolutely no relationship whatsoever to a curve of damage fluence versus pulse width. Therefore, the rejection based on Zinck is completely inappropriate.
- 29. In further support of the inappropriateness of the rejection on Zinck it is completely clear that the power levels at which Zinck is operating are so extremely low, melting of the metal surface is avoided. Therefore, at a minimum, Zinck and Miyauchi are inconsistent with one another. Therefore, for at least these reasons, rejection of independent claims 1 and 21 and dependent claims 8 through 11, 13 through 17, and 22 through 28 based on Zinck is not supportable.
- 30. Dependent claims 18, 20, and 38 were rejected as being unpatentable over Miyauchi in view of Kunz. Kunz does not even mention any operating conditions. Kunz does not have anything to do with LIB. It is inappropriate to attempt to combine Kunz with Miyauchi to try to arrive at our invention. For the reasons described above in connection with the discussion as to why Miyauchi does not define the key elements of the present invention, claims 18, 20, and 38 are also submitted to be patentable over the combination of Miyauchi and Kunz.

- 31. Claims 20 and 38 were rejected as being unpatentable over Miyauchi et al in view of Von Allmen et al. For the reasons described above in connection with the discussion as to why Miyauchi does not define the key elements of the present invention, claims 20 and 38 are also submitted to be patentable over the combination of Miyauchi and Von Allmen.
- 32. Von Allmen et al involved the use of nanosecond pulses to lase liquid zones created in a melt region that was previously exposed to a laser. Von Allmen et al show that a pulse should have a rapidly decreasing trailing edge in order that the liquid be effectively ejected from its puddle zone. They further teach that the trailing edge of the pulse should drop well below the material removal point in a time of approximately 100 nanoseconds. Von Allmen et al has a total pulse duration of about 5 microseconds. Since all of the operating conditions of Von Allmen et al are completely outside the ranges of the present invention, and since Von Allmen et al have absolutely nothing to do with LIB, it is inappropriate to attempt to combine Von Allmen with Miyauchi et al to try to arrive at our invention.
- 33. Claims 2, 12, and 19 which depend from claim 1, and claim 37 insofar as it depends on claims 1, 2, 5, and 21, and claim 39 were rejected as being unpatentable over Miyauchi et al in combination with Examiner's allegation that "It would have been obvious to adapt Miyauchi et al to provide this to efficiently create short high power laser pulses. Using laser pulses in the width time of femtoseconds to ablate metal is old and well known. It would have been obvious to adapt Miyauchi et al to provide this with high power spike pulses to ablate in small areas."

- As an expert in the field, I do not agree with 34. Examiner's supposition that those skilled in the art would have been able to adapt Miyauchi, create short high power laser pulses in accordance with the invention, use femtoseconds to ablate metal, and to ablate by LIB mechanism in small areas while essentially completely avoiding collateral damage as in the present invention. As stated earlier, Miyauchi does not remotely suggest the critical LIB mechanism; does not remotely suggest the threshold where the mechanism of thermal effects gives way to plasma controlled effects induced by LIB; does not essentially avoiding collateral damage as made possible by the very critical relationship which defines the "distinct and abrupt change of slope" region in the damage fluence versus laser pulse width threshold curve. Since Miyauchi completely misses the critical key features of the invention, there motivation for Miyauchi to combine amplification with the teachings of the independent claims. by the advantage of knowing what we have done in our invention is Examiner able to suppose that the invention should be done. I know of no suggestion as to how Miyauchi could be combined with a CPA apparatus to achieve the invention.
- Action Examiner summarizes many of the misunderstandings engendered in the previous Office Action items that form the foundation for the rejection including "that vaporization occurs which is necessary for plasma to be generated." This supposition shows a fundamental misunderstanding of the invention and the physics involved. Further, the statement that our previously presented arguments regarding gold are not relevant to aluminum, again show a fundamental misunderstanding of the invention, and of Miyauchi. Miyauchi states that there is definite relationship between the

U.S. Serial No. 08/224,961

transformation of laser energy into heat for "aluminum or the like." Therefore, Examiner's summary dismissal of our previously submitted arguments is inappropriate.

36. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements made jeopardize the validity of the application or any patent issued thereon.

Date: Oct 21, 1996

Peter P. Pronko

Attachments: Curriculum Vitae of Peter P. Pronko

PETER P. PRONKO

curriculum vitae

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EDUCATION:

Ph.D., Physics, University of Alberta (1966) M.S., Physics, University of Pittsburgh (1962) B.S., Physics, University of Scranton (Cum Laude - 1960)

EXPERIENCE:

- Nov. 1992 present: Associate Director (Industry Liaison), NSF Center for Ultrafast Optical Science; Research Scientist, Dept. Electrical Engineering & Computer Science, University of Michigan, Ann Arbor, Michigan
- 1984 1992 Director and Chief Scientist- Materials Research Division UES, Inc., Dayton, OH 45432
- 1982 1984 Chief Scientist Materials Research and Condensed Matter Physics Universal Energy Systems (UES), Inc., Dayton, OH 45432
- 1980 1982 Senior Physicist; Universal Energy Systems (UES), Inc., Dayton, OH
- 1972 1980 Physicist, Materials Science Division, Argonne National Lab, IL
- 1968 1972 Research Associate, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada
- 1966 1968 Assistant Professor of Physics, University of Scranton, Scranton, PA

HONORS, SCHOLARSHIP, AWARDS, AND ACCOMPLISHMENTS:

- * Post Doctoral Fellowship McMaster University, Institute for Materials Research, 1968–1970.
- * Presidential Internship at Argonne National Lab Illinois, 1972–1974.
- * Sabbatical Year at Solid State Division, Oak Ridge National Lab (1977–1978),
- * Co-organized Department of Energy Conference on Coatings for Materials Protection in Energy Systems (Argonne National Lab, 1979).
- * Symposium Co-organizer for Materials Research Society, Spring 1986 Conference in Anaheim, CA.
- * Served on organizing committee for the initiation of the MRS Journal of Materials Research.
- * Chairman of the Full Publications Committee for the Materials Research Society (MRS, Pittsburgh, PA), 1989–1991.
- * Member of Long Range Planning Committee for Materials Research Society 1991.
- * Co-author on four United States patent awards.
- * Chairman IEEE/LEOS Summer Topical Conference on "Advanced Applications of Lasers in Materials and Processing", Keystone, CO. (1996)
- * Listed in Who's Who in American Midwest, American Men and Women of Science, and Bohmiche Physicaliche Gesellshaft

MEMBERSHIP PROFESSIONAL SOCIETIES:

American Physical Society (APS), Materials Research Society (MRS), Institute of Electrical and Electronic Engineers (IEEE).